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Supporting Information

An Ionophore-Based Anion-Selective Optode Printed on Cellulose Paper

Xuewei Wang, Qi Zhang, Changwoo Nam, Michael Hickner, Mollie Mahoney, and Mark E. Meyerhoff**

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Author Contributions

X.W. Conceptualization: Lead; Data curation: Lead; Investigation: Lead; Methodology: Lead; Project administration: Equal; Writing—original draft: Lead; Writing—review & editing: Equal
Q.Z. Data curation: Equal; Investigation: Equal; Writing—original draft: Supporting
C.N. Data curation: Equal; Investigation: Equal; Writing—original draft: Supporting
M.H. Data curation: Equal; Investigation: Equal; Supervision: Equal
M.M. Data curation: Equal; Investigation: Equal
M.M. Conceptualization: Lead; Funding acquisition: Lead; Investigation: Equal; Methodology: Equal; Project administration: Equal; Supervision: Lead; Validation: Lead; Writing—original draft: Equal; Writing—review & editing: Lead.

Reagents and materials

Chromoionophore VI (ChVI; ETH 7075; 4′,5′-Dibromofluorescein octadecyl ester), Chromoionophore IV (ChIV; ETH 2412; 5-Octadecanoyloxy-2-(4-nitrophenylazo)phenol), chloride ionophore IV, tridodecylmethylammonium chloride (TDMAC), tetrahydrofuran, cyclohexanone, β-alanine, sodium salts of fluoride, chloride, bromide, chlorate, bromate, perchlorate, thiocyante, sulfate, acetate, phosphate dibasic, phosphate monobasic, nitrate, nitrite, and citrate, potassium iodide, and *trans*-1,2-diaminocyclohexane-N,N,N′,N′-tetraacetic acid (CDTA) were purchased from Sigma-Aldrich. Al(III) octaethylporphine chloride was obtained from Frontier Scientific, Inc. Whatman™ qualitative filter paper (grade 5) was purchased from Fisher Scientific. Scotch™ TP5851-100 thermal laminating pouches were obtained from Walmart.

Optode fabrication

F^- optode: 2.4 mg of Al(III) octaethylporphine chloride and 3 mg of ChVI were dissolved in 1 mL of cyclohexanone. This cocktail, as the ink, was printed onto Whatman qualitative filter paper by a Dimatix MP-2831 inkjet printer equipped with a Dimatix materials cartridge (DMC-11610, 10 pL drop size). Drop spacing was 25 µm and the number of printed layer was one. Both the cartridge nozzle and platen were at room tempareture. Maximum jetting frequency was set to 5k Hz.

Cl^- optode: 1.7 mg of tridodecylmethylammonium chloride, 1.6 mg of ChIV, and 3.6 mg of Cl^- ionophore IV (only for optode data shown in Figure 6B) were dissolved in 0.9 mL of cyclohexanone with 0.1 mL of tetrahydrofuran as the ink. Drop spacing was 15 µm. Other printing conditions were the same as those for the F^- optode.

Optode lamination

To laminate optodes, a piece of buffer-modified optode circle (1/4'' in diameter) was put into a laminating pouch and introduced into a Scotch™ thermal laminator. The temparature was set to be 120 °C (5 mil). Laminition was finished within seconds. Before use of the laminated optode for analytical measurements, two holes (1/16'' in diameter) were made by a Fiskars hand punch (Figure 5).

To meet the requirement of testing real drinking water, the β-alanine buffer used for the secondary modification of the optode employed to obtain the data in Figure 5 and Table S1 also contained 0.2 mM CDTA as a chelator of cations, such as Al^{3+} and Fe^{3+}, that could form complexes with F^-.[1]

Photography

Each optode paper was adhered to a piece of parafilm which was adhered to the back side of a transparent 96 well microtiter plate. Parafilm itself is adhesive and no extra adhesive material was used. The aqueous test solution only spread within optode area because of the high hydrophobicity of the underlying parafilm. Pictures for optodes were taken within a homemade black box by an iPhone 5S and the LED flash of the smartphone was used as the only light source.

Zeta potential test

An electrokinetic analyzer for solid surface analysis (Anton Paar, SurPASS) was used to measure the zeta potential for the various paper samples. The SurPASS gap cell accommodated samples with a rectangular size (2 cm x 1 cm) and the gap height was adjusted to 0.01 cm for all experiments. One mM KCl solutions with different amounts of HCl were used as the electrolyte in Figure S5A. β-alanine-phosphate buffer solutions (pH 3.6) with different concentrations of NaF were used as the electrolyte in Figure S5B. Before measurement, the flow rate (ml/min) for both flow directions was verified to provide a linear increase in pressure (up to 400 mbar). This linearity is an indicator for the proper evaluation of zeta potential. The zeta potential was determined from the streaming current measurement using the Smoluchowski equation.[2]

Physical characterization

X-ray photoelectron spectra were collected by a Kratos Ultra AXIS XPS with a monochromatic Al-Ka radiation source. Both survey scans (with a pass energy of 160 eV and a scan step of 1eV) and core scans on C1s (with a pass energy of 20 eV and a scan step of 0.05 eV) were collected. The spectra were calibrated by setting the C1s peak as 286.5 eV. Depth profiling analysis was performed using an argon ion sputtering gun operating at 4 keV (15 mA) and a raster size of 2 mm. All XPS data were analyzed by CasaXPS software. SEM images were collected on a JSM-7800F field emission scanning electron microscope (JEOL USA). Optical microscopy images were recorded using a Leica M80 stereomicroscope (Leica Mikrosysteme Vertrieb GmbH, Wetzlar, Germany). Water contact angles were measured at room temperature using a Cam 100 optical contact angle goniometer (KSV Instruments Ltd).

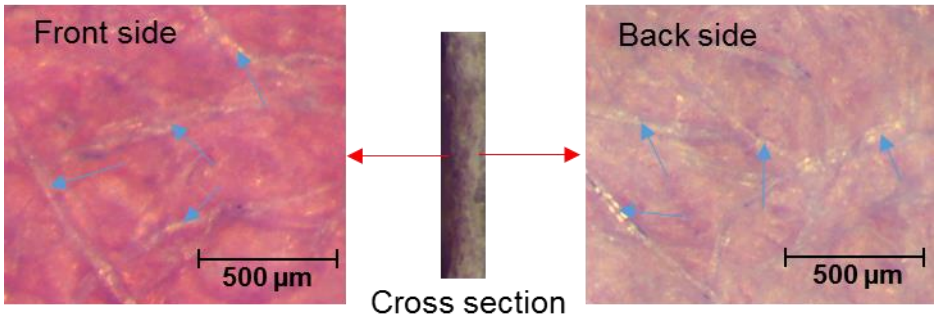

Figure S1. Microscopic images of the F^- optode from the front side (the side facing printer cartridge during printing), cross section and back side. The blue arrow indicates some large cellulose fibers.

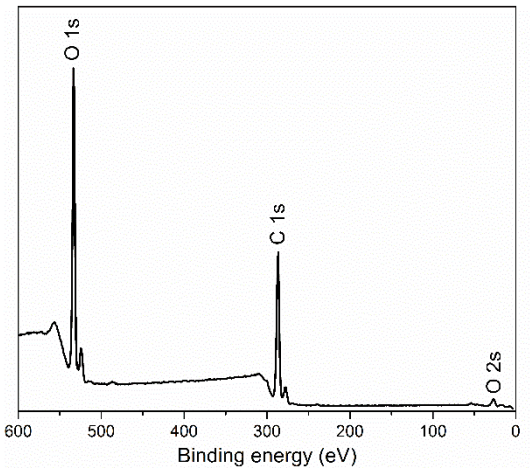

Figure S2. XPS survey scan of raw filter paper.

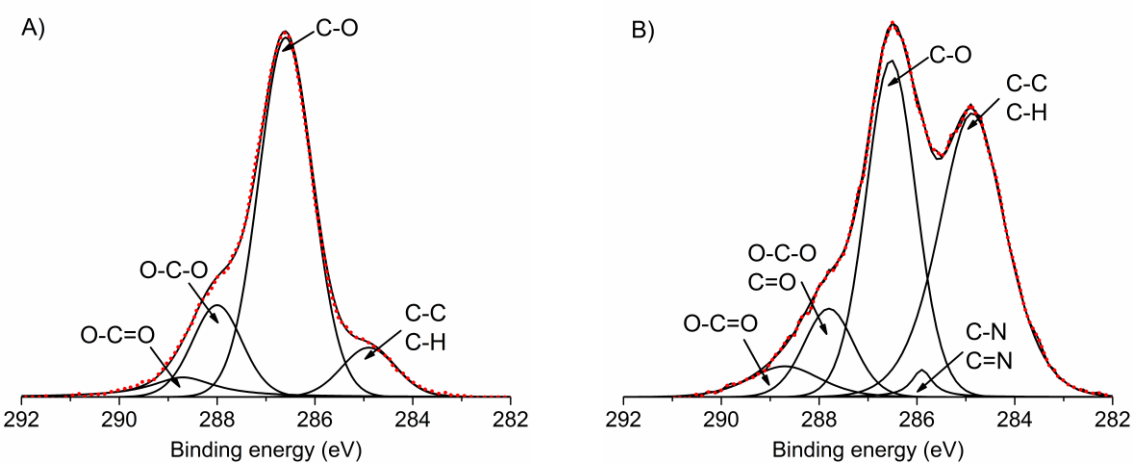

Figure S3. XPS C1s core scan of raw filter paper (A) and F^- optode (B). The O-C=O peak in raw filter paper is due to the presence of a low amount of carboxyl groups.[3]

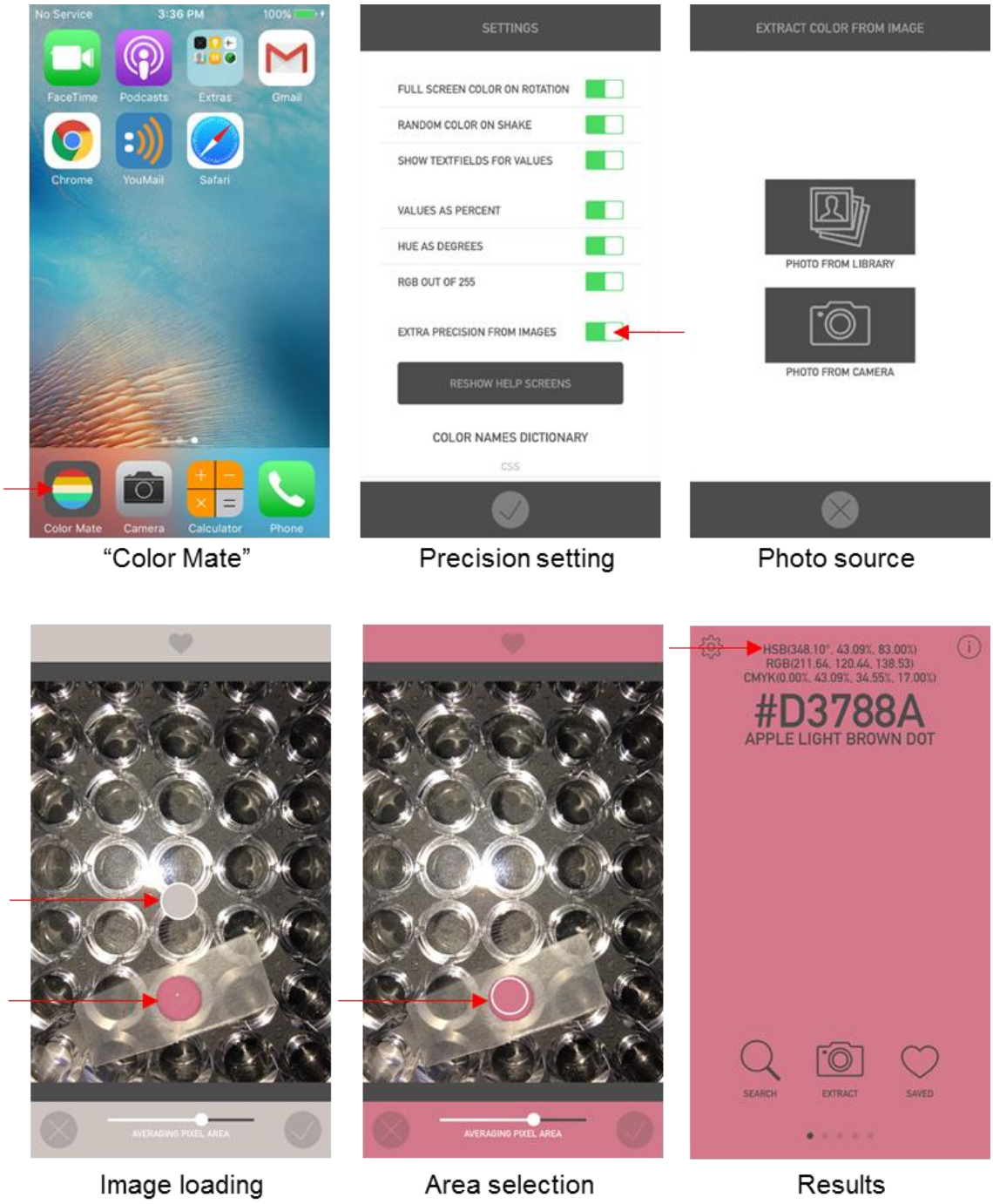

Figure S4. Procedure of extraction of "hue" from the optode by using an iPhone 5S with "Color Mate - Convert and Analyze Colors" app (https://itunes.apple.com/us/app/color-mate-convert-and-analyze-colors/id896088941?mt=8). The used pixel area is 26 rather than the maximum area, 40. The white circle shown in the picture is the maximum area and the selected area will be seen as a smaller circle within this big circle. A selected area significantly smaller than the optode circle was found to yield more reliable hue results because the actual selected area is a square rather than a circle (although shown as a circle) according to David Williames, the designer of this app.

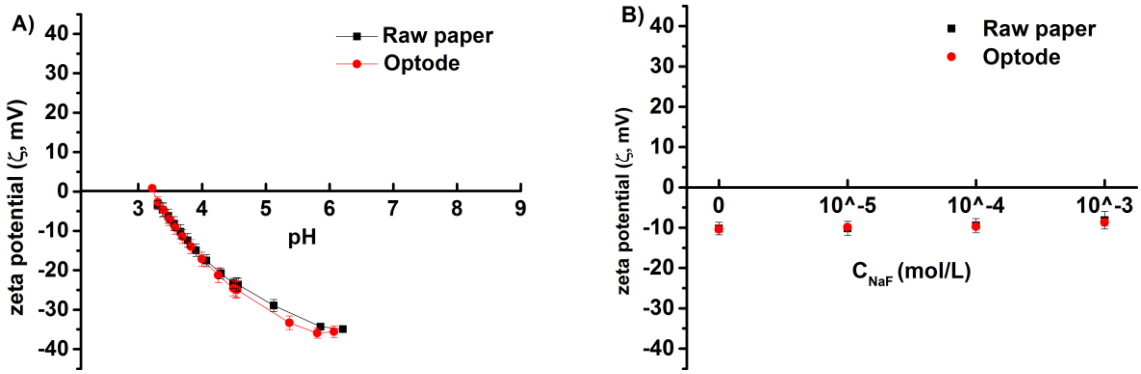

Figure S5. A) Zeta potential of raw filter paper and F^- optode at different pH values. The negative potential is due to the carboxyl groups on cellulose.[3] B) Zeta potential of raw filter paper and F^- optode in pH 3.6 β-alanine buffer with different concentrations of added NaF.

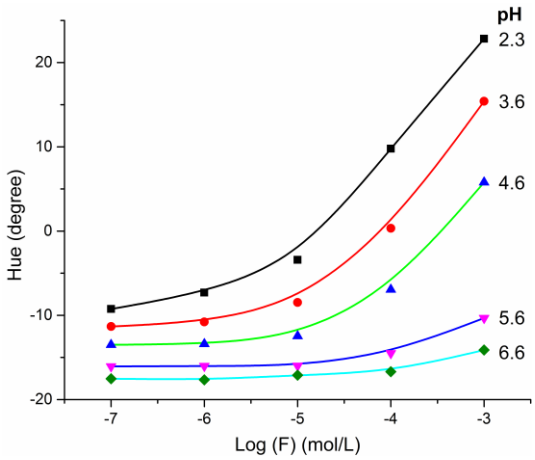

Figure S6. Calibration curves of F^-/HF at different sample pH values.

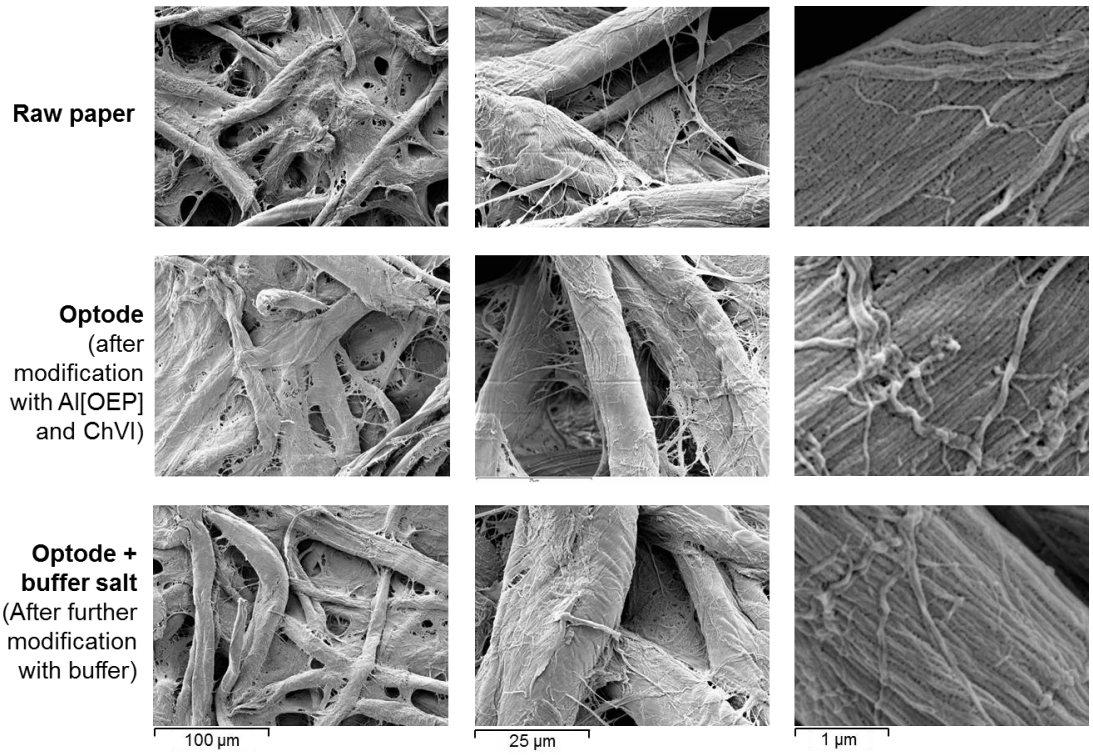

Figure S7. SEM images of raw filter paper, F^- optode, and F^- optode modified with dry buffer (β-alanine-phosphate buffer at pH 3.6).

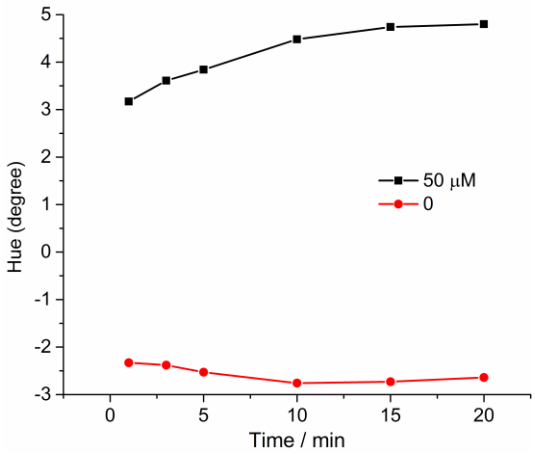

Figure S8. Hue-time curves of the final optodes wetted in DI water (Red line) and DI water containing 50 µM NaF (Black line).

Table 1. Comparison of F^- concentrations of two Ann Arbor drinking water samples tested by the proposed optode and LaF_3 membrane ISE (Cole-Parmer Combination Fluoride-Selective Electrodes) and recovery rates of spiked F^- in these drinking water samples. The sample was tested directly by optode without any pre-treatment. In contrast, for ISE test, the sample was mixed with total ionic strength adjuster (Cole-Parmer Replacement ionic strength adjustor) according to the manual of the Cole-Parmer Fluoride-Selective Electrodes.

Sample	**Optode (μM)**	**ISE (μM)**	**Percent error**	**Recovery rate**
#1	29.4 ± 1.7	31.7	7.3 %	
#1+25 μM	54.7 ± 3.0			101.6 %
#1+50 μM	81.8 ± 4.1			104.8 %
#2	33.0 ± 2.4	36.1	8.6 %	
#2+25 μM	57.4 ± 3.8			97.6 %
#2+50 μM	78.5 ± 2.9			91.0 %

Table S2. Cost of reagents and materials of one F^- optode strip

Reagent or material	**Amount of reagent/material per strip**	**Unit price**	**Cost per strip**	**Total cost**
ChVI	1.5 μg	$592/100 mg	0.9 cent	
Al[OEP]	1.2 μg	$240/100 mg	0.3 cent	
β-alanine	45 μg	$54.9/500 g	<0.01 cent	
Phosphoric acid (85%)	17 nL	$244/500 mL	<0.01 cent	**~1.2 cent**
CDTA	0.91 μg	$123/50 g	<0.01 cent	
Filter paper	32 mm^2	$0.69/26880 mm^2	<0.01 cent	
Laminating pouch	~2 cm^2	$0.06/60 cm^2	<0.01 cent	

References:

[1] I. H. Badr, M. E. Meyerhoff, *Anal. Chem.* **2005**, *77*, 6719-6728.

[2] H. Xie, T. Saito, M. A. Hickner, *Langmuir* **2011**, *27*, 4721–4727

[3] A. Murphy, B. Gorey, K. de Guzman, N. Kelly, E. P. Nesterenko, A. Morrin, *RSC Adv.* **2015**, *5*, 93162-93169.